

Method of Producing Comb or Star Copolymers Using Epoxy-Functionalized Nitroxylethers

The synthesis of amphiphilic block- and graft copolymers containing both unpolar and polar chain species of different chemical nature has been approached by several techniques. A promising approach for the synthesis of aliphatic polyether backbones has been described, for example, by Heitz et al. in Macromol. Chem. 183, 1685 (1982).

One problem, especially in the design of graft copolymers, is the lack of grafting efficiency, especially if a radical "grafting to" process is chosen. Complete grafting of the graft monomer is seldom achieved and hence the final product is always contaminated with homopolymer formed in the grafting step. This process is mostly applied in the synthesis of high impact polystyrene, where styrene is grafted radically onto a polybutadiene latex. More efficient grafting is achieved when active sites within the polymeric backbone are used to covalently attach new polymer chains to the starting molecule. This requires, however, the presence of well-defined "initiation points" in the backbone.

Linear polyethers based on ethylene oxide and/or propylene oxide, besides their vast application in polyurethanes, find numerous applications in pharmaceutical and biomedical applications. Industrial applications include amongst numerous others flocculating agents in the treatment of industrial waste water, drag reduction and the modification of surface properties, such as the use as antistatic agents. Linear block copolymers of ethylene and propylene oxide also have commercial applications and serve as non-ionic tensides, emulsifiers and stability improvers (as for example "Pluronics®" manufactured by BASF). Also statistical copolymers of this type are accessible. Most of these products are liquids or waxes, depending on their final molecular weight. These copolymers are still water soluble with a minimum content of 25% ethylene oxide and hence pose an interesting class of materials for the synthesis of amphiphilic graft copolymers.

Besides ethylene oxide, propylene oxide and monomers derived therefrom, epichlorohydrine forms polyethers, which are used as specialty rubbers.

The present invention provides a method of attaching a polymeric side chain to a polymer backbone differing in polarity and chemical structure therefrom and forming a comb or star polymer structure. This represents a new method in the synthesis of comb or star

copolymers combining two separate polymerization processes. The properties of polyethers can now be combined with those of typical thermoplastic polymers. In addition a new class of initiators for the synthesis of star polymers is provided.

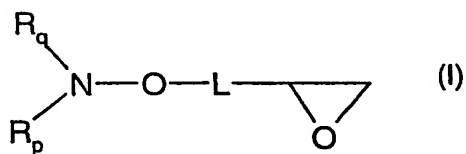
In particular the process provides a method of polymerizing in a first step a polymer backbone from epoxy group containing monomers and in a second step polymerizing under controlled radical conditions a comb or star structure onto this backbone.

The described process allows alternatively the access to comb or star polymers. Star copolymers are achieved for example if the polymer chain consists of a short chain length for example 3 to 5 units. Comb copolymers are mainly obtained at prolonged chain lengths or if random copolymers are synthesized. The number of grafts can then be adjusted by the concentration of comonomers.

The resulting copolymer structures are of interest in surface modification applications of thermoplastic materials, insuring a permanent polar surface by anchoring the polar moiety via the less polar polymer chains in the matrix of the desired resin. Similarly, these polymers can be used as nonionic surfactants. The incorporation of the novel molecules into a backbone polymer containing epichlorohydrine can lead to rubber-thermoplastic comb copolymers.

One aspect of the invention is a method for the preparation of a comb or star copolymer comprising

a) polymerising in a first step one or more epoxy group containing monomers to obtain a polyether, wherein at least one monomer is of formula (I)



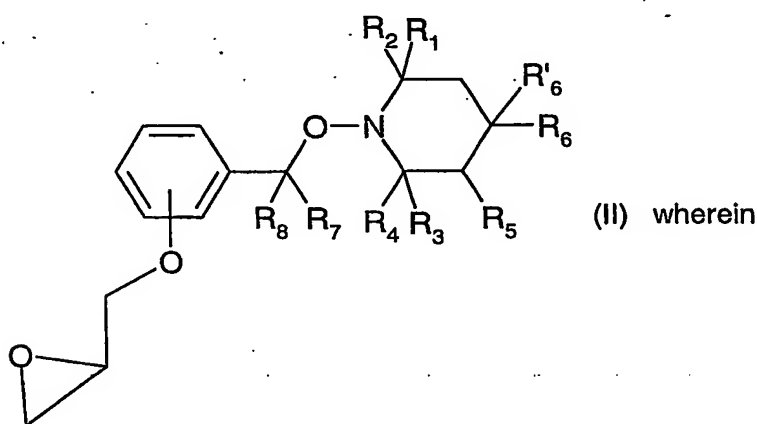
wherein L is a linking group selected from the group consisting of C₁-C₁₈alkylene, phenylene, phenylene-C₁-C₁₈alkylene, C₁-C₁₈alkylene-phenylene, C₁-C₁₈alkylene-phenylene-oxy and C₅-C₁₂cycloalkylene;

R_p and R_q are independently tertiary bound C₄-C₂₈alkyl groups which are unsubstituted or substituted by one or more electron withdrawing groups or by phenyl; or

R_p and R_q together form a 5 or 6 membered heterocyclic ring which is substituted at least by 4 C_1 - C_4 alkyl groups and which may be interrupted by a further nitrogen or oxygen atom; and in a second step

b) adding to the polymer obtained in step a) at least one ethylenically unsaturated monomer, heating the resulting mixture to a temperature where cleavage of the nitroxylether bond occurs and radical polymerization starts; and polymerizing to the desired degree.

For example the monomer according to formula I is of formula (II)



R_1 , R_2 , R_3 and R_4 are independently of each other C_1 - C_4 alkyl;

R_5 is hydrogen or C_1 - C_4 alkyl;

R'_6 is hydrogen and R_6 is H, OR_{10} , $NR_{10}R_{11}$, $-O-C(O)-R_{10}$ or $NR_{11}-C(O)-R_{10}$;

R_{10} and R_{11} independently are hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkinyl or C_2 - C_{18} alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} alkylene bridge interrupted by at least one O atom; or

R_6 and R'_6 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein

R_{20} is H, straight or branched C_1 - C_{18} alkyl, C_3 - C_{18} alkenyl or C_3 - C_{18} alkinyl, which may be unsubstituted or substituted, by one or more OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl;

C_5 - C_{12} cycloalkyl or C_5 - C_{12} cycloalkenyl;

phenyl, C_7 - C_9 phenylalkyl or naphthyl which may be unsubstituted or substituted by one or more C_1 - C_8 alkyl, halogen, OH, C_1 - C_8 alkoxy, carboxy, C_1 - C_8 alkoxycarbonyl;

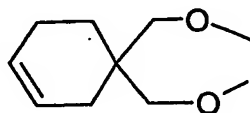
$-C(O)-C_1-C_{36}$ alkyl, or an acyl moiety of a α,β -unsaturated carboxylic acid having 3 to 5 carbon atoms or of an aromatic carboxylic acid having 7 to 15 carbon atoms;

$-\text{SO}_3\text{Q}^+$, $-\text{PO}(\text{OQ}^+)_2$, $-\text{P}(\text{O})(\text{OR}_2)_2$, $-\text{SO}_2\text{R}_2$, $-\text{CO-NH-R}_2$, $-\text{CONH}_2$, COOR_2 , or $\text{Si}(\text{Me})_3$, wherein Q^+ is H^+ , ammonium or an alkali metal cation; or

R_6 and R_6' are independently $-\text{O-C}_1\text{-C}_{12}\text{alkyl}$, $-\text{O-C}_3\text{-C}_{12}\text{alkenyl}$, $-\text{O-C}_3\text{-C}_{12}\text{alkinyl}$, $-\text{O-C}_5\text{-C}_8\text{cycloalkyl}$, $-\text{O-phenyl}$, $-\text{O-naphthyl}$, $-\text{O-C}_7\text{-C}_9\text{phenylalkyl}$; or

R_6 and R_6' together form one of the bivalent groups $-\text{O-C}(\text{R}_{21})(\text{R}_{22})\text{-CH}(\text{R}_{23})\text{-O-}$, $-\text{O-CH}(\text{R}_{21})\text{-CH}_{22}\text{-C}(\text{R}_{22})(\text{R}_{23})\text{-O-}$, $-\text{O-CH}(\text{R}_{22})\text{-CH}_2\text{-C}(\text{R}_{21})(\text{R}_{23})\text{-O-}$, $-\text{O-CH}_2\text{-C}(\text{R}_{21})(\text{R}_{22})\text{-CH}(\text{R}_{23})\text{-O-}$, $-\text{O-o-phenylene-O-}$, $-\text{O-1,2-cyclohexyliden-O-}$,

$-\text{O-CH}_2\text{-CH=CH-CH}_2\text{-O-}$ or



; wherein

R_{21} is hydrogen, $\text{C}_1\text{-C}_{12}\text{alkyl}$, COOH , $\text{COO-(C}_1\text{-C}_{12})\text{alkyl}$ or $\text{CH}_2\text{OR}_{24}$;

R_{22} and R_{23} are independently hydrogen, methyl ethyl, COOH or $\text{COO-(C}_1\text{-C}_{12})\text{alkyl}$;

R_{24} is hydrogen, $\text{C}_1\text{-C}_{12}\text{alkyl}$, benzyl, or a monovalent acyl residue derived from an aliphatic, cycloaliphatic or aromatic monocarboxylic acid having up to 18 carbon atoms; and

R_7 and R_8 are independently hydrogen or $\text{C}_1\text{-C}_{18}\text{alkyl}$.

$\text{C}_1\text{-C}_{18}\text{alkyl}$ can be linear or branched. Examples are methyl, ethyl, propyl, isopropyl, butyl, 2-butyl, isobutyl, t-butyl, pentyl, 2-pentyl, hexyl, heptyl, octyl, 2-ethylhexyl, t-octyl, nonyl, decyl, undecyl, dodecyl or octadecyl. Where up to $\text{C}_{36}\text{alkyl}$ is possible, $\text{C}_1\text{-C}_{18}\text{alkyl}$ is preferred.

Alkyl substituted by a group $-\text{COOH}$ is for example $\text{CH}_2\text{-COOH}$, $\text{CH}_2\text{-CH}_2\text{-COOH}$, $(\text{CH}_2)_3\text{-COOH}$ or $\text{CH}_2\text{-CHCOOH-CH}_2\text{-CH}_3$

Hydroxyl- or alkoxy carbonyl substituted $\text{C}_1\text{-C}_{18}\text{alkyl}$ can be, for example, 2-hydroxyethyl, 2-hydroxypropyl, methoxycarbonylmethyl or 2-ethoxycarbonylethyl.

Alkenyl having from 2 to 18 carbon atoms is a branched or unbranched radical, for example propenyl, 2-butenyl, 3-butenyl, isobutenyl, n-2,4-pentadienyl, 3-methyl-2-butenyl, n-2-octenyl, n-2-dodecenyl, isododecenyl.

Alkinyl having from 2 to 18 carbon atoms is a branched or unbranched radical, for example propinyl, 2-butylinyl, 3-butylinyl, isobutylinyl, n-2,4-pentadiinyl, 3-methyl-2-butylinyl, n-2-octinyl, n-2-dodecinyl, isododecinyl.

Examples of alkoxy are methoxy, ethoxy, propoxy, isopropoxy, butoxy, isobutoxy, pentoxy, isopentoxy, hexoxy, heptoxy or octoxy.

C₇-C₉phenylalkyl is for example benzyl, α -methylbenzyl, α,α -dimethylbenzyl or 2-phenylethyl, benzyl is preferred.

C₅-C₁₂cycloalkyl is for example cyclopentyl, cyclohexyl, cycloheptyl, methylcyclopentyl or cyclooctyl.

C₅-C₁₂cycloalkenyl is for example 3-cyclopentenyl, 3-cyclohexenyl or 3-cycloheptenyl.

Examples of a monocarboxylic acid having up to 18 carbon atoms are formic acid, acetic acid, propionic acid, the isomers of valeric acid, methyl ethyl acetic acid, trimethyl acetic acid, capronic acid, lauric acid or stearic acid. Examples for unsaturated aliphatic acids are acrylic acid, methacrylic acid, crotonic acid, linolic acid and oleic acid.

Typical examples of cycloaliphatic carboxylic acids are cyclohexane carboxylic acid or cyclopentane carboxylic acid.

Examples of aromatic carboxylic acids are benzoic acid, salicylic acid or cinnamic acid.

Halogen is F, Cl, Br or I.

C₁-C₁₈alkylene is a branched or unbranched radical, for example methylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, hexamethylene, heptamethylene, octamethylene, decamethylene or dodecamethylene.

C₂-C₁₂alkylene bridges interrupted by at least one O atom are, for example, -CH₂-O-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-CH₂-CH₂-, -CH₂-O-CH₂-CH₂-O-CH₂-.

Alkoxy carbonyl is for example methoxycarbonyl, ethoxycarbonyl, propoxycarbonyl.

Preferably R₁, R₂, R₃, R₄ are methyl, or R₁ and R₃ are ethyl and R₂ and R₄ are methyl, or R₁ and R₂ are ethyl and R₃ and R₄ are methyl.

For instance R_5 is hydrogen or methyl.

In particular R'_6 is hydrogen and R_6 is H, OR_{10} , $NR_{10}R_{11}$, $-O-C(O)-R_{10}$ or $NR_{11}-C(O)-R_{10}$;

R_{10} and R_{11} independently are hydrogen, C_1 - C_{18} alkyl, C_2 - C_{18} alkenyl, C_2 - C_{18} alkinyl or C_2 - C_{18} alkyl which is substituted by at least one hydroxy group or, if R_6 is $NR_{10}R_{11}$, taken together, form a C_2 - C_{12} alkylene bridge or a C_2 - C_{12} alkylene bridge interrupted by at least one O atom; or

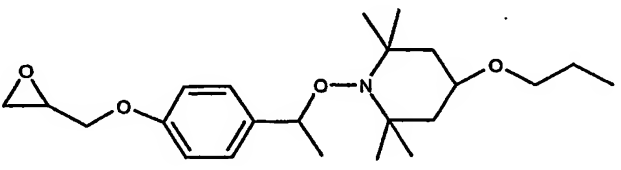
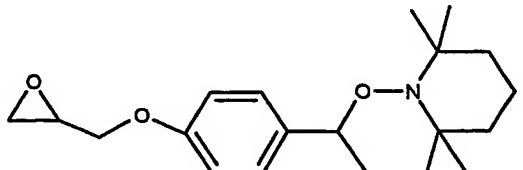
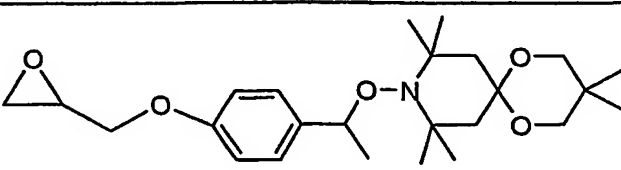
R_6 and R'_6 together are both hydrogen, a group $=O$ or $=N-O-R_{20}$ wherein

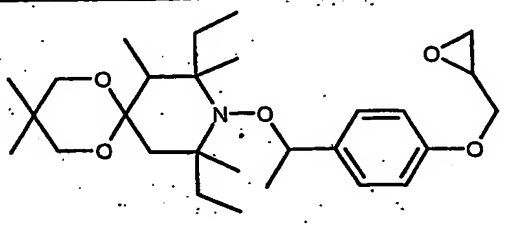
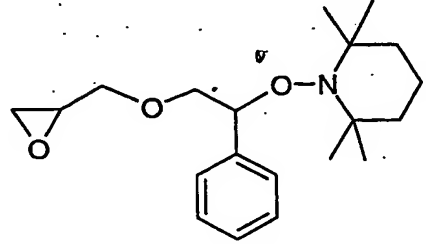
R_{20} is H or straight or branched C_1 - C_{18} alkyl.

In another preferred embodiment of the invention R_6 and R'_6 together form one of the bivalent groups $-O-C(R_{21})(R_{22})-CH(R_{23})-O-$, $-O-CH(R_{21})-CH_2-C(R_{22})(R_{23})-O-$, $-O-CH(R_{22})-CH_2-C(R_{21})(R_{23})-O-$, $-O-CH_2-C(R_{21})(R_{22})-CH(R_{23})-O-$ and R_{21} , R_{22} and R_{23} have the meaning as defined above.

Specific compounds are given in Table A

Table A

Compound Number	Structure
101	
102	
103	

104	
105	

The compounds of formula II and in particular the compounds given in Table A are known and may be prepared as described in WO 99/46261, WO 02/48109 or US 5 721 320.


Examples of suitable other epoxy functional monomers  which can be used as comonomers are given in Table B.

Table B

Name	CAS No.	X
Ethylene oxide	75-21-8	H
Propylene oxide	75-56-9	CH ₃
2,3-Epoxypropyl-phenylether	122-60-1	CH ₂ -O-C ₆ H ₅
2,3-Epoxypropyl-4-nonyl-phenylether	6178-32-1	CH ₂ -O-C ₆ H ₅ -C ₉ H ₁₉
Epichlorohydrine	106-89-8	-CH ₂ -Cl
2,3-Epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether	19932-27-5	CH ₂ -O-CH ₂ -(CF ₂) ₃ CHF ₂

For instance the epoxy group containing a monomer different from that of formula I is selected from the group consisting of ethylene oxide, propylene oxide, 2,3-epoxypropyl-

phenylether, 2,3-epoxypropyl-4-nonyl-phenylether, epichlorohydrine and 2,3-epoxypropyl-2,2,3,3,4,4,5,5-octafluoropentylether.

These compounds are known and commercially available.

Preferably the weight ratio of the monomers of formula I or formula II to the sum of other monomers is from 99:1 to 1:99, particularly 80:20 to 20:80, specifically 75:25 to 25:75.

The general polymerization procedure of step a) is well known and for example described in Encyclopedia of Polymer Science and Technology, Vol 6, 1967, 103-209.

There are principally two different processes. The first depends upon the tendency of the oxiran group to oxyalkylated active-hydrogen sites in the presence of Lewis acids or Lewis bases as catalysts. The second type of polymerization reaction involves the rapid polymerization of the oxiran group to high molecular weight polymers on a catalytic surface in a heterogeneous reaction system. Other initiation systems are described in Odian, "Principles of polymerization", Wiley-Interscience New York, 1991, pp.536 and Houben Weyl, Makromolekulare Stoffe, Bd. E20/2, Thieme Stuttgart, 1987, pp 1367. They include furthermore aluminium porphyrin compounds and certain iron and zinc complexes as catalysts.

The polymerization can be carried out in bulk or in solution, containing 10-90% (by vol.) solvent, the latter especially if gaseous monomers (propylene oxide or ethylene oxide) are used. Suitable solvents include tetrahydrofuran (THF), benzene, toluene, acetonitrile, dimethylformamide (DMF), chlorinated solvents and mixtures thereof. If the backbone contains a high fraction of ethylene oxide, also water or mixtures of water with suitable organic solvents can be used.

Suitable Lewis bases are for example alkali metal alcoholates.

The polyether polymer of step a) has for example an average weight molecular weight of M_w 1000 to 100 000, preferably from 2000 to 50 000.

The reaction temperature should be kept preferably as low as possible since cleavage of the nitroxylether bond depends on the chemical structure and may occur at temperatures above

100° C. The polymerization temperature should therefore not exceed 100° C. A suitable polymerization temperature is for example from 10° to 80° C, preferably from 30° to 70° C. Polymerization is normally carried out under inert gas atmosphere at normal atmospheric pressure.

Since lower reaction temperatures are applied reaction time is usually longer, typically from 1-72 hours, in particular 1-48 hours, preferably 2-24 hours.

The isolation of the polyether backbone polymer depends on its molecular structure. Residual monomer can be removed in vacuo at temperatures not exceeding 100°C if they are liquid, extracted (for example via Soxhlet extraction) or washed with appropriate solvents if they are solid.

Preferably the ethylenically unsaturated monomer or oligomer added in step b) is selected from the group consisting of styrene, substituted styrene, conjugated dienes, vinyl acetate, vinylpyrrolidone, vinylimidazole, maleic anhydride, (alkyl)acrylic acid anhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles, (alkyl)acrylamides, vinyl halides or vinylidene halides.

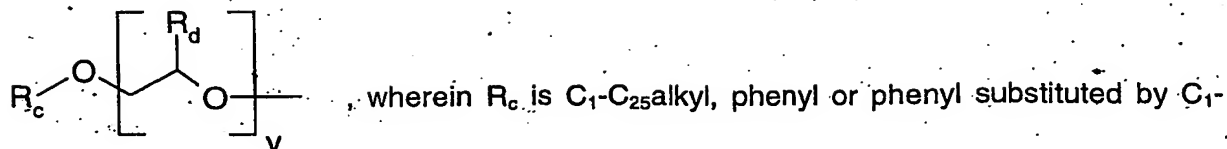
Particularly the ethylenically unsaturated monomers are isoprene, 1,3-butadiene, α -C₅-C₁₈alkene, styrene, α -methyl styrene, p-methyl styrene or a compound of formula $\text{CH}_2=\text{C}(\text{R}_a)-(\text{C}=\text{Z})-\text{R}_b$, wherein R_a is hydrogen or C₁-C₄alkyl, R_b is NH₂, O⁻(Me⁺), glycidyl, unsubstituted C₁-C₁₈alkoxy, C₂-C₁₀₀alkoxy interrupted by at least one N and/or O atom, or hydroxy-substituted C₁-C₁₈alkoxy, unsubstituted C₁-C₁₈alkylamino, di(C₁-C₁₈alkyl)amino, hydroxy-substituted C₁-C₁₈alkylamino or hydroxy-substituted di(C₁-C₁₈alkyl)amino, -O-CH₂-CH₂-N(CH₃)₂ or -O-CH₂-CH₂-N⁺H(CH₃)₂ An⁻;

An⁻ is a anion of a monovalent organic or inorganic acid;

Me is a monovalent metal atom or the ammonium ion.

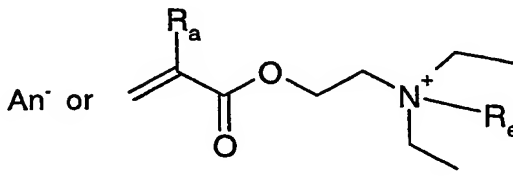
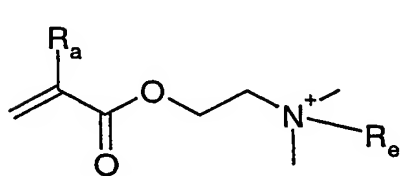
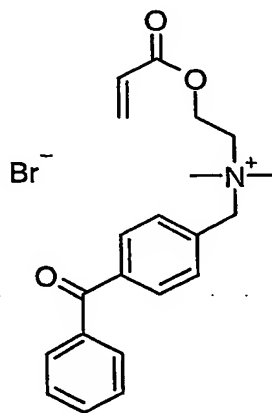
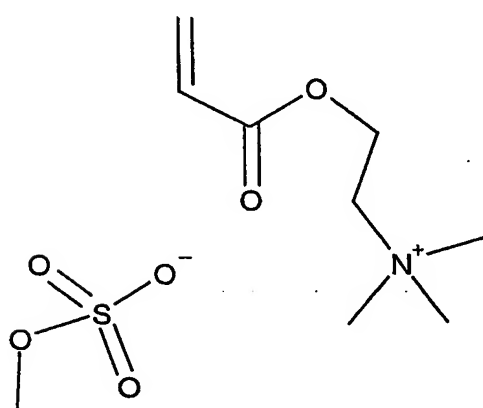
Z is oxygen or sulfur.

Examples for R_a as C₂-C₁₀₀alkoxy interrupted by at least one O atom are of formula



C_{18} alkyl, R_d is hydrogen or methyl and v is a number from 1 to 50. These monomers are for example derived from non ionic surfactants by acrylation of the corresponding alkoxyated alcohols or phenols. The repeating units may be derived from ethylene oxide, propylene oxide or mixtures of both.

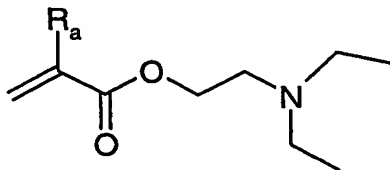
Further examples of suitable acrylate or methacrylate monomers are given below.

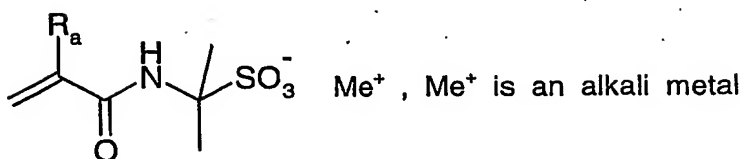
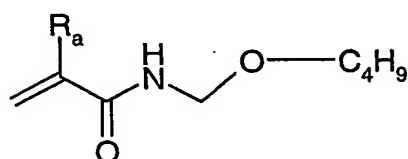
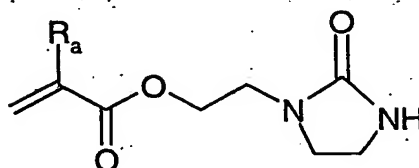
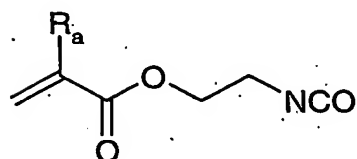
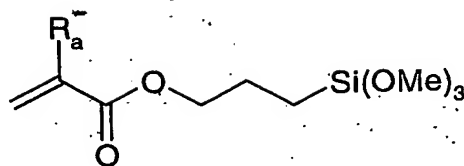
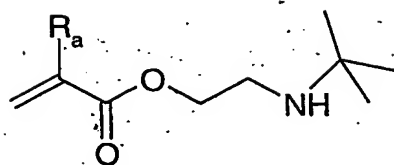


An⁺, wherein An⁺

and R_a have the meaning as defined above and R_e is methyl, benzyl or benzoylbenzyl. An⁺ is preferably Cl⁻, Br⁻ or ⁻O₃S-O-CH₃.

Further acrylate monomers are

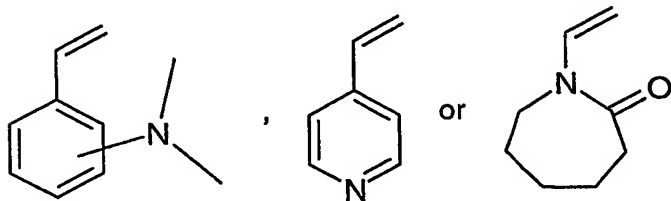
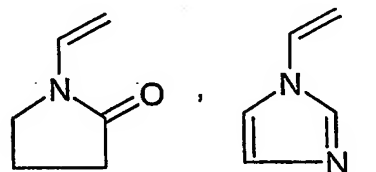




Me^+ , Me^+ is an alkali metal

cation or the ammonium cation.

Examples for suitable monomers other than acrylates are



Preferably R_a is hydrogen or methyl, R_b is NH_2 , glycidyl, unsubstituted or with hydroxy substituted $\text{C}_1\text{-C}_4$ alkoxy, unsubstituted $\text{C}_1\text{-C}_4$ alkylamino, $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})$ amino, hydroxy-substituted $\text{C}_1\text{-C}_4$ alkylamino or hydroxy-substituted $\text{di}(\text{C}_1\text{-C}_4\text{alkyl})$ amino; and Z is oxygen.

Particularly preferred ethylenically unsaturated monomers are styrene, methylacrylate, ethylacrylate, butylacrylate, isobutylacrylate, tert. butylacrylate, hydroxyethylacrylate, hydroxypropylacrylate, dimethylaminoethylacrylate, methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, hydroxyethyl(meth)acrylate, hydroxypropyl(meth)acrylate,

dimethylaminoethyl(meth)acrylate, acrylonitrile, acrylamide, methacrylamide or dimethylaminopropyl-methacrylamide.

For example the weight ratio between the polyether prepared in step a) and the ethylenically unsaturated monomer added in step b) is from 90:10 to 10:90.

As already mentioned the nitroxylether bond cleaves at elevated temperature and radical polymerization is initiated. Preferably in step b) the polymerization temperature is from 80° C to 160° C, in particular from 100° C to 140° C.

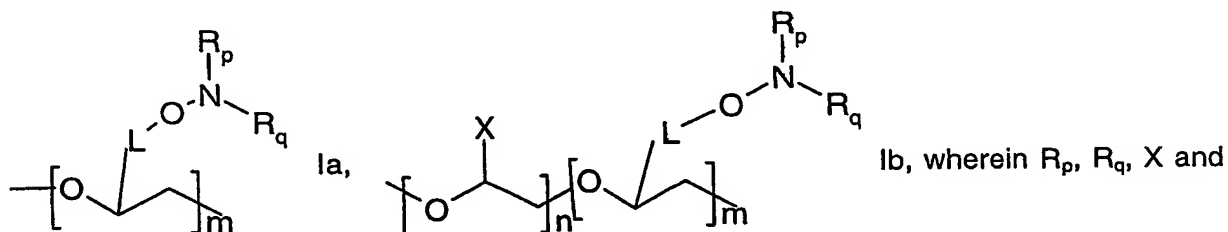
Typically the average weight molecular weight M_w is from 2000 to 300 000, preferably from 3000 bis 100000.

The polydispersity index of the resulting comb or star copolymer is typically between 1.1 and 3.0.

A further aspect of the invention is a composition comprising a compound of formula II as defined above, at least one epoxy functional monomer different from that of formula II and optional water or an organic solvent or mixtures thereof.

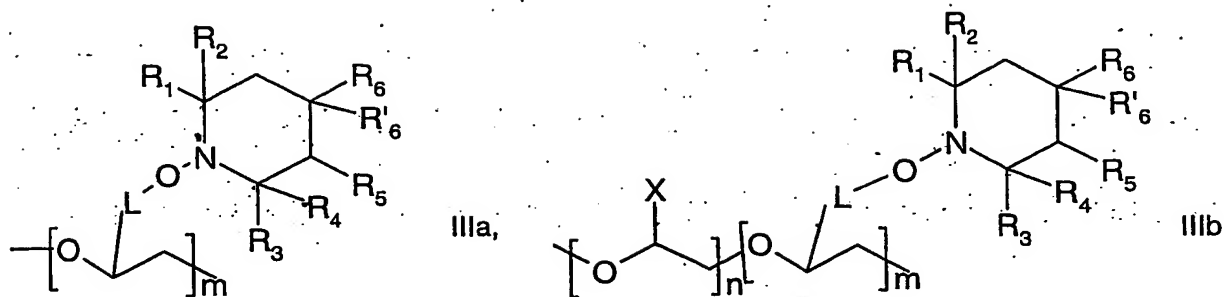
Yet another aspect of the invention is a polyether obtainable according to step a) of the method described above.

This polyether has an idealized repetitive structural element of formula Ia or Ib



L are as defined above and n and m are independently a number from 10 to 1000.

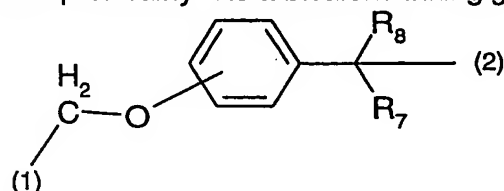
In particular the polyether has an idealized repetitive structural element of formula IIIa or IIIb



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , R'_6 and L are as defined above, m and n are independently a number from 10 to 1000 and

X is H , CH_3 , $CH_2-O-C_6H_5$, $CH_2-O-C_6H_5-C_9H_{19}$, CH_2Cl or $CH_2-O-CH_2-(CF_2)_3CHF_2$.

Most preferably L is a bivalent linking group of formula



wherein (1) denotes the bond to the polymer

backbone and (2) denotes the bond to the oxygen atom of the nitroxyl radical; R_7 and R_8 are as defined above.

Further subjects of the invention are a comb or star copolymer obtainable according to the method as described above and the use of a polyether with pending nitroxylether groups for the preparation of a comb or star copolymer.

For instance the ethylenically unsaturated monomer forming the comb or star is selected from the group consisting of styrene, substituted styrene, (alkyl)acrylic acidanhydrides, (alkyl)acrylic acid salts, (alkyl)acrylic esters, (meth)acrylonitriles and (alkyl)acrylamides.

Definitions for the individual substituents have already been given for the method of preparation of comb or star copolymers, they apply also to the other aspects of the invention.

The polymers prepared by the present invention are useful for following applications: forming parts, extrusion or injection moldings, plastic materials for shaping parts with for example improved processibility and/or barrier properties, adhesives, detergents, dispersants, emulsifiers, surfactants, defoamers, adhesion promoters, corrosion inhibitors, viscosity

improvers, lubricants, rheology modifiers, thickeners, crosslinkers, paper treatment, water treatment, electronic materials, paints, coatings, photography, ink materials, imaging materials, superabsorbants, cosmetics, hair products, preservatives, biocide materials or modifiers for asphalt, leather, textiles, ceramics and wood.

Because the polymerization of step b) is a "quasi living" polymerization, it can be started and stopped practically at will. Furthermore, the polymer product retains the functional alkoxyamine group allowing a continuation of the polymerization in a living matter. Thus, in one embodiment of this invention, once the first monomer is consumed in the initial radical polymerizing step a second monomer can then be added to form a second block on the growing polymer chain in a second polymerization step. Therefore it is possible to carry out additional polymerizations with the same or different monomer(s) to prepare multi-block copolymers.

Furthermore, since this is a "quasi living" radical polymerization, blocks can be prepared in essentially any order. One is not necessarily restricted to preparing block copolymers where the sequential polymerizing steps must flow from the least stabilized polymer intermediate to the most stabilized polymer intermediate, such as is the case in ionic polymerization. Thus it is possible to prepare a multi-block copolymer in which a polyacrylonitrile or a poly(meth)acrylate block is prepared first, then a styrene or butadiene block is attached thereto, and so on.

Random copolymers and tapered copolymer structures can be synthesized as well by using a mixture of monomers or adding a second monomer before the first one is completely consumed.

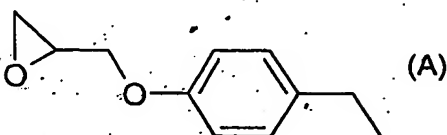
Yet another aspect of the invention is the use of a comb or star copolymer obtainable according to the method described above as adhesive, surface modifier, surfactant or compatibilizer in thermoplastic, elastic or thermosetting polymers or as plastic material for extrusion or injection molding for shaping parts.

The following examples illustrate the invention.

Examples (V1 and V2) prove the polymerizability of the epoxy group

Compound A is the precursor molecule in the synthesis for the epoxy-group containing nitroxyl ethers.

Compound A is known and prepared according to standard methods.



In order to test its principal ability of polymerizing under Lewis base catalysis compound A is subjected to an anionic polymerization using potassium – *tert.* – butylate.

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.56 g (0.02 mol) compound A (liquid) are dissolved in 5 ml dry toluene (Merck). 210 mg (1.82 mmol) potassium – *tert.* – butylate are added and the homogeneous solution is heated for 6 hours at 110°C. After cooling to room temperature, 2 ml of methanol are added via syringe and subsequently the solvents are removed in vacuo. The product is obtained as a colorless wax (V1).

NMR analysis confirms the formation of a polyether due to the presence of the characteristic signals –O-CH₂-CH-. Furthermore the absence of monomer is confirmed.

Molecular weights are determined by GPC in tetrahydrofurane (THF) on a HP 1090 device equipped with an RI and UV detector, using a solvent flow of 1 ml/min. Columns are calibrated using polystyrene standards.

The same experiment is successfully repeated with 1 mmol potassium – *tert.* – butylate as Initiator (V2). Table 1 lists polymer yields and molecular weight data. The “living nature” of this type of polymerization is confirmed by the different molecular weights obtained when using different amounts of initiator.

Table 1

Example	Conversion Compound A (%)	M _n (calc.)	M _n (GPC)	M _w	M _w /M _n
V1	92	1840	2500	3900	1.58
V2	82	3280	3500	6600	1.88

Example E1-E14: Preparation of the polyether backbone polymer with pending nitroxylether groups

Example E1

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 40 g (0.1 mol) compound 101 (light brown oil), 30 g (0.18 mol) compound A and 4 g (0.036 mol) potassium - tert. - butylate are dissolved in 100 ml dry toluene. The light yellow solution is heated at 60°C for 18 hours. After the addition of 2 ml methanol solvents are removed in vacuo and the product is dried overnight in vacuo at room temperature. The product is obtained as a highly viscous brown oil.

Example E2

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 20 g (0.05 mol) compound 101 (light brown oil), 30 g (0.18 mol) compound A and 4 g (0.036 mol) potassium - tert. - butylate are dissolved in 100 ml dry toluene. The light yellow solution is heated at 60°C for 18 hours. After the addition of 1 ml methanol solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as a viscous yellow oil.

Example E3

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.35 g (0.01 mol) compound 102 (colorless oil), 7.12 g (0.04 mol) compound A and 0.41 g (0.0036 mol) potassium - tert. - butylate are dissolved in 10 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as very viscous yellow oil.

Example E4

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 3.35 g (0.01 mol) compound 102 (colorless oil), 3.56 g (0.02 mol) compound A and 0.41 g (0.0036 mol) potassium - tert. - butylate are dissolved in 10 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as light yellow oil.

Example E5

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.051 mol) compound 102 (colorless oil), 14 g (0.051 mol) 2,3-epoxypropyl-4-nonylphenylether (techn., Sigma-Aldrich, CAS # 6178-32-1) and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as a light brown oil.

Example E6

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.051 mol) compound 102 (colorless oil), 7 g (0.025 mol) 2,3-epoxypropyl-4-nonylphenylether and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as light brown oil.

Example E7

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 17 g (0.0 mol) compound 102 (colorless oil), 28 g (0.101 mol) epoxypropyl-4-nonylphenylether and 1 g (0.009 mol) potassium - tert. - butylate are dissolved in 60 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol, solvents are removed in vacuo and the product dried overnight in vacuo at room temperature. The product is obtained as brown oil.

Example E8

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid) and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 30 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow solid.

Example E9

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 1.78 g (0.01 mol) compound A and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 40 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow solid.

Example E10

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 3.57 g (0.02 mol) compound A and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 40 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow solid.

Example E11

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 7.14 g (0.04 mol) compound A and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 40 ml dry toluene. The solution is heated at 80°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow solid.

Example E12

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 2.76 g (0.01 mol) 2,3-epoxypropyl-4-nonylphenylether and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 50 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow solid.

Example E13

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 5.52 g (0.02 mol) 2,3-epoxypropyl-4-nonylphenylether and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 50 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow, high viscous oil.

Example E14

In a dry, Argon-purged Schlenk tube equipped with a rubber septum, a magnetic stir bar and an Argon inlet, 8.67 g (0.02 mol) compound 103 (white solid), 11.06 g (0.02 mol) 2,3-epoxypropyl-4-nonylphenylether and 0.55 g (0.0045 mol) potassium - tert. - butylate are dissolved in 50 ml dry toluene. The solution is heated at 60°C for 6 hours. After the addition of 1 ml methanol solvents are removed in vacuo. Then the product is precipitated in methanol and dried overnight in vacuo at room temperature. The product is obtained as slight yellow, high viscous oil.

Table 2 summarizes the yields and the molecular weight data of the obtained products. Polymer yield is determined gravimetrically after drying or precipitating of the products.

Table 2: Molecular weights and conversion data

Example	Polymer yield (%)	M _n (GPC)	M _w	M _w /M _n
E1	97	3500	7500	2.08
E2	97	2500	5000	2.00
E3	98	4500	12400	2.70
E4	99	2900	7600	2.63
E 5	not determined	2500	3700	1.46
E 6	n.d.	2300	3000	1.33
E 7	n.d.	2500	3300	1.31
E 8	99	2700	3300	1.22
E 9	99	3400	4100	1.21
E 10	99	3500	4200	1.20
E 11	99	4300	5200	1.21

E 12	99	3100	3700	1.19
E 13	99	2700	3300	1.22
E 14	99	1800	2300	1.28

Preparation of comb copolymers by reinitiation

Example E15

In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E5 are dissolved in 50 g (0.48 mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Example E16

In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E6 are dissolved in 50 g (0.48 mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath and heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Example E17

In a dry Schlenk tube equipped with a stopcock, magnetic stirbar and an Argon inlet, 5 g of the polymer of example E7 are dissolved in 50 g (0.48 mol) of freshly distilled styrene (Merck). The solution is degassed by three consecutive freeze-thaw cycles and purged with argon. The tube is then immersed in an oil bath and heated at 130°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is analyzed by GPC. The graft copolymer yield is determined gravimetrically.

Example E18

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E8 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is

then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as white solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E19

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E9 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E20

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E10 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E21

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E11 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is

obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E22

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E12 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E23

In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E13 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Example E24

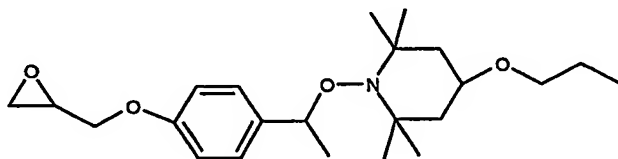
In a dry 200ml-autoclave (Fa. Büchi) equipped with a stirrer and an Argon inlet 2.5 g of the polymer of example E14 are dissolved in a mixture of 45 g (0.43 mol) styrene (Merck) and 15 g (0.28 mol) acrylonitrile. The solution is degassed and purged with argon. The autoclave is then immersed in an oil bath and heated at 110°C for 6 hours. After cooling to room temperatures, volatiles are removed in vacuo and the crude reaction product is precipitated in methanol. After drying over night in vacuo at roomtemperature the graft copolymer is obtained as slight yellow solid. The graft copolymer is analyzed by GPC and the yield is determined gravimetrically.

Table 3 summarizes the yields and the molecular weight data of the obtained graft copolymers. Molecular weights are determined as described above.

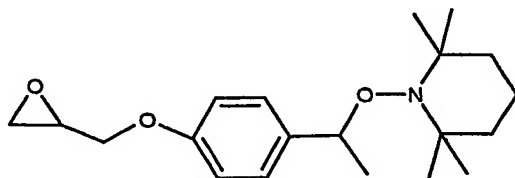
Table 3: Molecular weights and styrene or styrene/acrylonitrile conversion

Example	% styrene or styrene/acrylonitrile grafted onto backbone	M _n (GPC)	M _w	M _w /M _n
E 15	22	4600	6500	1.42
E 16	7	4100	5600	1.38
E 17	15	3700	8700	2.33
E 18	55	42500	53000	1.25
E 19	61	50500	63200	1.25
E 20	53	44900	58800	1.31
E 21	63	61500	87200	1.41
E 22	47	43100	52900	1.23
E 23	52	40000	54600	1.37
E 24	41	35300	48300	1.37

Compound 101

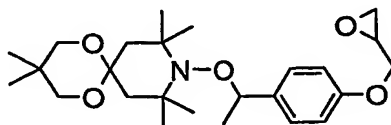


Compound 102



Both compounds are prepared according to WO 99/46261, examples A1 and A5.

Compound 103



Copound 103 is prepared as described in WO 02/48109.